Preparation of 1-Monoglycerides by Interesterification

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High yields (84-92 per cent) of 1-monoglycerides are obtained by reacting 1,2-isopropylideneglycerol with methyl esters of pure lauric, myristic, palmitic, stearic and oleic acids in the presence of sodium methoxide as a catalyst at 140-90° for 1 hr. On crystallization, the crude product gives TLC pure 1-monoglycerides in 80 per cent yields.

THE preparation of high purity 1-monoglycerides was simplified first by Hartman[1] by carrying out esterification of 1,2-isopropylideneglycerol (IPG) with free fatty acids in the presence of *p*-toluenesulphonic acid as a catalyst. Anfinsen and Perkins[2] simplified this procedure still further by replacing the aqueous phase collection apparatus of Hartman with a soxhlet. By using chloroform in place of benzene as a carrier liquid and anhydrous magnesium sulphate as absorbent for water formed during the reaction, they were able to reduce the time of reaction by about 40 per cent in the case of monoglycerides of unsaturated fatty acids and by as much as 70 per cent for monoglycerides of saturated acids. As an example, acylation of IPG with lauric acid was shown to be complete in 3·5 hr as against 13 hr required in Hartman's procedure.

Where fatty acids of desired purity are available, they are directly used for esterification. However, where high purity acids are either not easily available or are very expensive, the crude fatty acids are normally purified by fractional distillation of their methyl esters. Therefore, hydrolysis of the desired ester fraction becomes an essential step in the preparation of monoglycerides by Hartman's method. To eliminate this step, it was of interest to study the reaction between IPG and methyl esters of fatty acids leading to acid migration, formation of IPG ester and liberation of MeOH.

While reviewing the methods of synthesizing 1-monoglycerides, Mattson and Volphenhein[3] have shown the possibility of using interesterification. However, the per cent yields of 1-monoglycerides by this method have not been mentioned and, therefore, its comparison with the other two methods (use of fatty acids and fatty acid chlorides which are known to give as much as 90 per cent conversion), is not possible.

Preliminary experiments using chloroform, hexane, or benzene as a carrier liquid and either *p*-toluenesulphonic acid or sodium methoxide as a catalyst gave poor conversions. Since quick removal of the liberated methanol would expedite the reaction, experiments were carried out at temperatures higher than 100°C. and in the absence of any solvent medium.

The IPG was readily prepared in bulk by Hartman's method. The acidic catalyst was neutralized by Na_2CO_3 and the solvent evaporated. The crude IPG was purified by distillation under low pressure; b.p. 82°/8 mm. (approx.).

Weighed quantities of IPG and sodium methoxide were introduced into a two-necked flask having an inlet for nitrogen, a thermometer dipping into the mixture and an outlet for nitrogen. After the desired temperature was reached, the ester was added. Immediately, the reaction mass started boiling and copious vapours were evolved. Samples were taken periodically to find out the degree of conversion with progress of the reaction and dissolved in ethyl ether and the ethereal solutions after washing with water and cooling in an ice-bath hydrolysed as usual to obtain crude monoglycerides. The 1-monoglyceride contents of the crude products were estimated by the method of Pohle and Mehlenbacher[4].

A large number of experiments, first with methyl myristate and then with esters of different acids (Table 1), were carried out varying the quantity of esters (10-50 g.), excess IPG (20-200 per cent), temperature of reaction (140° to 190°C.), time of reaction (15 min. to 4 hr) and proportion of catalyst (0·5-2·0 per cent on ester weight).

The crude monoglycerides were purified by crystallization from their ethereal solutions at 5°C.; yield 80 per cent (on the weight of the crude product).

The course of reaction in some cases was followed by TLC by spotting the reaction products as such on a silica-coated plate which was developed in a ternary solvent system consisting of petroleum ether-ethyl ether-acetic acid (70: 30:1, vol./vol.). The spots were localized by either iodine absorption or charring with chromic acid. An intermediate reaction product gave four distinct spots corresponding to methyl ester, IPG ester, fatty acid and IPG. With the reaction going to completion, the methyl ester spot almost vanished while the spot corresponding to acylated IPG enlarged. Crystallized 1-monoglycerides gave only one spot with the same solvent system.

The total monoglyceride contents[5] of a few crude products were invariably found to be higher by

Table 1 — Influence of Temperature and Amount of Catalyst on the Conversion of Different Esters

(Ester, 10 g.; IPG, 200 per cent excess; reaction period, 1 hr)

Reaction temp. °C.	Ester	1-Monoglyceride content (%) in the products* using	
		2 per cent NaOMe	0·5 per cent NaOMe
140	Methyl laurate	91·7	86·5
100	Methyl myristate	55·0	—
140	do	86·5	—
160	do	92·0	90·5
180	do	89·0	—
160	Methyl palmitate	62·4	—
180	do	94·5	94·0
160	Methyl stearate	87·0	—
180	do	—	94·5
190	do	91·3	—
180	Methyl oleate	—	84·7

*Uncrystallized product.

2-7 units than the 1-monoglyceride contents. This obviously showed the presence of 2-monoglycerides in the crude products.

The reaction between IPG and methyl esters studied here is akin to alcoholysis involving the complex monohydric alcohol, viz. IPG and the simple methyl ester. The optimum temperature of reaction increases with increase in molecular weight of the ester. At temperatures 140-90° the conversion is very high as indicated by the high 1-monoglyceride contents (Table 1).

A part of the ester gets converted into soap by the action of sodium methoxide. This soap was recovered in the water washings of the ethereal solution of the reaction product. The aqueous soap solution was acidified and the liberated fatty acids recovered. They were found to be equivalent to the amount of catalyst used.

Where IPG is already available, the alcoholysis method studied here has certain advantages over the direct condensation of free fatty acids. These are (i) the use of esters directly eliminating the hydrolysis step, (ii) saving time, (iii) absence of a solvent and (iv) simplicity of equipment. These more than counterweigh the higher temperatures employed for the reaction.

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